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(54) REMOVEABLE, TEMPORARY PRINTING PASTE

(57) The present invention relates to a removable, temporary printing paste particularly suitable for printing textile. The present invention further relates to a method for manufacturing the printing paste as well as to the method for printing the printing paste onto a substrate, in particular onto textile. Further encompassed is a method of removing the printing paste from the substrate.



Figure 1b

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a removable, temporary printing paste particularly suitable for printing textile. The present invention further relates to a method for manufacturing the printing paste as well as to the method for printing the printing paste onto a substrate, in particular onto textile. Further encompassed is a method of removing the printing paste from the substrate.

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BACKGROUND OF THE INVENTION

[0002] Textile waste is a well-known problem nowadays, since for the production of textiles, many resources are needed (e.g. water, chemicals etc.). Therefore, it is tried to establish a circular economy to upcycle textile waste such that it can be re-used again.

[0003] However, this regularly means that from the textile waste, only e.g. fractional parts can be recovered and upcycled again such that new textile can be produced again.

[0004] Often the textiles thrown away are not damaged, but merely do not fit the taste of the consumer (any longer). Often textiles are in fact only used once for special occasions (e.g. special events) because there are prints on the textile for just these special occasions.

[0005] There is therefore the need to provide a possibility to remove such special prints from textile or also other substrates such that it can be used again.

OBJECTS OF THE INVENTION

[0006] The objection of the present application is therefore to provide a printing paste which can be easily removed from textile.

SUMMARY OF THE INVENTION

[0007] The object is solved by the following items: Item 1: A printing paste comprising:

- a) at least one liquid selected from water, alcohols or a mixture thereof;
- b) at least one alkali metal salt or earth alkali metal salt selected from carbonates or sulfates or a mixture thereof;
- c) at least one natural polymer selected from cellulose, cellulose derivatives, polysaccharides, collagens or mixtures thereof.

Item 2: Printing paste according to item 1, wherein the printing paste comprises additives selected from the group comprising proteins, fatty substances, sugars, waxes, pigments or mixtures thereof.

Item 3: Printing paste according to items 1 or 2, wherein the weight ratio of the at least one liquid to

the at least one alkali metal salt or earth alkali metal salt to the at least one natural polymer is in the range of at least 10:4:1, or at least 12:4:1, or at least 15:4:1, or at least 20:4:1, or at least 24:4:1, and at most 100:16:1, or at most 96:16:1, or at most 90:16:1, or at most 50:8:1, or at most 48:8:1.

Item 4: Printing paste according to at least one of items 1 to 3, wherein the printing paste comprises

- a) water:
- b) earth alkali metal carbonate or sulfate selected from calcium carbonate (CaCO3), magnesium carbonate (MgCO3), barium sulfate (BaSO4) or a mixture thereof;
- c) cellulose or cellulose derivates selected from methylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose, ethylmethyl cellulose, carboxymethyl cellulose or mixtures thereof;
- d) optionally at least one pigment. Item 5: Method for manufacturing the printing paste as disclosed in at least one of items 1 to 4 comprising the steps of
- i) mixing the at least one liquid and the at least one earth alkaline salt to form a slurry;
- ii) homogenization of the slurry obtained in step
- i), while adding the at least one natural polymer;
- iii) further homogenization of the composition obtained in step ii);

iv) swelling of the homogenized composition obtained in step iii) to obtain the printing paste;

v) optionally mixing and homogenizing at least one additive.

Item 6: Method as disclosed in item 5, wherein step iv) is conducted for at least 5 minutes, or for at least 10 minutes, or for at least 15 minutes, or for at least 20 minutes, or for at least 25 minutes, or for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 90 minutes.

Item 7: Use of the printing paste according to at least one of items 1 to 4 or use of the printing paste as manufactured according to items 5 or 6 for printing a substrate.

Item 8: Use as claimed in item 7, wherein the substrate is selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics; preferably textile.

Item 9: Method for printing a substrate with the printing paste according to at least one of the items 1 to 4 or with the printing paste as manufactured in items 5 or 6 comprising:

- i) Printing the printing paste onto the substrate to obtain a printed substrate;
- ii) Drying the printed substrate.

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Item 10: Method as disclosed in item 9, wherein the drying is conducted at a temperature of at least 25 °C, or at least 30°C, or at least 40°C, or at least 50°C, or at least 60°C, or at least 70°C, or at least 80°C, or at least 90°C, or at least 110°C, or at least 120°C, or at least 130°C.

Item 11: Substrate printed with the printing paste as disclosed in at least one of the items 1 to 4 or the printing paste as manufactured in items 5 or 6; or substrate as obtained according to the method as disclosed in items 9 or 10.

Item 12: Substrate as disclosed in item 11, wherein the substrate is selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics; preferably textile.

Item 13: Method for removing the printing paste as disclosed in at least one of the items 1 to 4 or the printing paste as manufactured in items 5 or 6 from the printed substrate as disclosed in items 11 or 12, or as obtained according to the method disclosed in items 9 or 10 comprising

i) subjecting the printed substrate to a cleaning step, wherein in the cleaning step water and at least one cleaning agent is used.

Item 14: Method according to item 13, wherein the cleaning agent is selected from soaps or laundry detergents, or mixtures thereof

Item 15: Method according to item 13 or 14, wherein the cleaning step is conducted for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 80 minutes, or for at least 90 minutes, or for at least 100 minutes, or for at least 110 minutes.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The object is solved by a printing paste comprising or consisting of at least one liquid selected from water, alcohol or a mixture thereof; at least one (earth) alkali metal salt, selected from carbonates or sulfates or a mixture thereof; at least one natural polymer selected from cellulose, cellulose derivatives, polysaccharides, collagens or mixtures thereof.

[0009] The advantage of the printing paste according to the invention is that the printing paste is easily removable from the substrate onto which the paste is printed without leaving residues on the substrate. A further advantage of the printing paste according to the invention is, that the printing paste is environmentally friendly. A further advantage is, that the printing paste according to the invention, although being easily removable in a cleaning step, nevertheless is fixed enough to the substrate to withstand e.g. sweat or rain during use.

[0010] Under the term "printing paste" as used within the context of the present application, a composition is

to be understood which is used for providing prints onto substrates, preferably textile. In essence, the printing paste can be regarded as a suspension, i.e. as mixture of solids and fluids, wherein the mixture is preferably homogeneous. The modification of the paste can reach from liquid form to a solid-like form, depending on the applied printing method (e.g. if the printing method is normal painting it is best to use the printing paste in a liquid form, whereas when the printing method is silk screen printing, then it is more advantageous to use the printing paste in a solid-like form). By adjusting the content of the at least one liquid, the desired modification of the printing paste can be achieved.

[0011] The printing paste according to the invention comprises at least one liquid selected from water, alcohol or a mixture thereof. The water can be tap water or purified water. The alcohol can be selected from any commonly known alcohol, like C1 to C10 alkyl alcohols, e.g. methanol, ethanol or propanol, wherein ethanol is the preferred alcohol. Water is preferred to be used as at least one liquid.

[0012] The printing paste according to the invention comprises further at least one (earth) alkali metal salt selected from carbonates or sulfates. Under the term "(earth) alkali metal salts" as used within the context of the present application, salts are understood in which alkali cations, earth alkali cations or mixtures of both are contained. Under alkali cations Li+, Na+, K+ cations are to be understood, preferably Na+ and K+, most preferred Na⁺. Under earth alkali cations, in particular, Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺ cations are to be understood, preferably Mg²⁺, Ca²⁺, and Ba²⁺, most preferred Ba²⁺. Under the term "sulfates", a sulfate salt is to be understood containing an SO₄3- anion and as cations for balancing the negative charges, alkali cations, earth alkali cations or mixtures of both. Under the term "carbonate", a carbonate salt is to be understood, containing an CO₃²⁻ anion and as cations for balancing the negative charges, alkali cations, earth alkali cations or mixtures of both. Preferred (earth) alkali metal salt selected from carbonates or sulfates to be used in the printing paste according to the invention are magnesium carbonate (CAS nbs.: 546-93-0, 13717-00-5, 5145-48-2, 14457-83-1, 61042-72-6; e.g. as magnesia chalk; e.g. available from Diacleanshop),

calcium carbonate (e.g. as chalk), barium sulfate (e.g. as baryte) or mixtures thereof. It is advantageous that the (earth) alkali metal salt is used in form of powder, preferably a fine powder.

[0013] The printing paste according to the invention comprises further at least one natural polymer selected from cellulose, cellulose derivatives, polysaccharides, collagens, or mixtures thereof. Under the term "cellulose derivates" as used within the context of the present application, cellulose compounds are to be understood which are based on cellulose, but chemically modified, e.g. cellulose esters or cellulose ethers. Preferably such cellulose derivatives are selected from food additives.

Suitable cellulose derivates can be selected from methylhydroxyethyl cellulose (e.g. commercially available as Tylose® from Kremer Pigmente; CAS nb.: 9032-42-2), hydroxypropyl cellulose (e.g. commercially available as Klucel[™] H from Kremer Pigmente; EINECS-Nb.: 618-388-0), methyl cellulose, hydroxypropylmethyl cellulose, ethylmethyl cellulose, carboxymethyl cellulose or mixtures thereof. Suitable polysaccharides can be selected from starches, like potatoe starch, tapioca starch, corn starch or the like. Further suitable polysaccharides can be selected from pectin or algin as well. Suitable collagens can be selected from rabbit skin glue or gelatine. Preferably, methylhydroxyethyl cellulose, hydroxypropyl cellulose, starches, algin, pektin, gelatine, rabbit skin glue or mixtures thereof are used as natural polymer in the printing paste.

[0014] The printing paste according to the invention can further comprise additives selected from the group comprising proteins, fatty substances, sugars, waxes, pigments or mixtures thereof. The additives can determine the final appearance of the printing paste on the substrate. E.g. since the printing paste according to the invention is colorless, pigments can be used to provide a coloured printing paste. All commonly known pigments are suitable to be used in the printing paste according to the invention. The pigments can be used in powder form or in liquid form. Further the pigments can be natural pigments or synthetic pigments. Preferably pigments are used which are also used to colour food. Commercially available pigments are known as Texprint-AQ. To provide a glossy appearance to the printing paste according to the invention, when applied onto the substrate, proteins (e.g. egg white), fatty substances like cremes; sugars (e.g. glucose or saccharose or dextrose) or waxes (e.g. paraffin wax) can be added into the printing paste according to the invention. The amount of such additives for proving a glossy appearance can vary from at least 0.01 % by weight, or at least 0.1 % by weight, or at least 0.2% by weight, or at least 0.4% by weight, up to at most 1% by weight, or at most 0.8% by weight, or at most 0.7% by weight. Amounts in % by weight are in each case based on the total weight of the printing paste according to the invention. Suitable amounts of pigment can at least 0.01% by weight, or at least 0.02 % by weight, or at least 0.5% by weight or at least 1% by weight, or at least 3% by weight, or at least 5% by weight, or at least 7% by weight, or at least 9% by weight, or at least 10 % by weight, or at least 12 % by weight, or at least 15% by weight. In essence, the amount of pigment used is determined by the desired color grade which should be achieved in the printing paste according to the invention. If small amounts of pigment are used, the color of the printing paste according to the invention will be very light, pastel shades. If high amount of pigment is used in the printing paste according to the invention, the color of the printing paste will be very intense. Amounts in % by weight are in each case based on the total weight of the printing paste according to the invention.

[0015] The printing paste according to the invention can comprise or consists of water, earth alkali carbonate or earth alkali sulphate selected from calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), barium sulfate (BaSO₄) or a mixture thereof; cellulose or cellulose derivates selected from methylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose, ethylmethyl cellulose, carboxymethyl cellulose or mixtures thereof and optionally at least one pigment and/ or at least a fatty substance.

[0016] The printing paste according to the invention can comprise or consists of water, earth alkali carbonate selected from calcium carbonate (CaCO₃), magnesium carbonate (MgCOs) or a mixture thereof; cellulose derivates selected from methylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropylmethyl cellulose, ethylmethyl cellulose, carboxymethyl cellulose or mixtures thereof and optionally at least one pigment and/ or a fatty substance.

[0017] The printing paste according to the invention can comprise or consists of water, earth alkali carbonate selected from magnesium carbonate (MgCOs); cellulose derivates selected from methylhydroxyethyl cellulose and optionally at least one pigment.

[0018] The printing paste according to the invention can comprise or consists of water, earth alkali carbonate selected from magnesium carbonate (MgCOs); cellulose derivates selected from methylhydroxyethyl cellulose and at least one pigment.

[0019] In the printing paste according to the invention, the weight ratio of the at least one liquid to the at least one alkali metal salt or earth alkali metal salt to the at least one natural polymer is in the range of at least 10:4:1, or at least 12:4:1, or at least 15:4:1, or at least 20:4:1, or at least 24:4:1, and at most 100:16:1, or at most 96:16:1, or at most 90:16:1, or at most 50:8:1, or at most 48:8:1. The weight ratio of liquid: (earth) alkali metal salt: natural polymer is in the range of 10:4:1 to 100:16:1, or 12:4:1 to 1:16:96. As mentioned above, depending on the modification of the printing paste according to the invention, the weight ratios of liquid: (earth) alkali metal salt: natural polymer can be chosen. E.g. the weight ratio 48:8:1 results in a liquid modification of the printing paste according to the invention and is thus suitable if the printing paste is used as paint to color the substrate. E.g. the weight ratio 24:4:1 results in a more solid-like printing paste according to the invention and is thus suitable to be used in silk screen printings, pad printing, stamp printing and the like.

[0020] Further, the present invention encompasses a method for manufacturing the Method for manufacturing the printing paste according to the invention comprising the steps of

- i) mixing the at least one liquid and the at least one (earth) alkaline salt to form a slurry;
- ii) homogenization of the slurry obtained in step i), while adding the at least one natural polymer;

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- iii) further homogenization of the composition obtained in step ii);
- iv) swelling of the homogenized composition obtained in step iii) to obtain the printing paste;
- v) optionally mixing and homogenizing at least one additive.

[0021] Once step iv) or v) is finalized, the printing paste according to the invention is ready for use, i.e., ready for being applied to the substrate.

[0022] Further, it is possible that additional steps are conducted prior to or after step i), prior to or after step ii), prior to or after step iii), prior to or after step iv), or prior to or after step v). Possible steps are for example heating steps, cooling steps, sieving steps.

[0023] It is possible to conduct step ii) immediately after step i). It is also possible to store the slurry obtained in step i) for a certain time, before conducting step ii). It is possible to conduct optional step v) directly after step iv), or to store the printing paste obtained in step iv) for a certain time before conducting step v).

[0024] The temperature of the liquid used in step i) can be ambient temperature or elevated temperature, e.g. 30°C, 35°C, 40°C, 45°C, 50°C or higher.

[0025] The mixing occurs by adding the at least one liquid to the at least one (earth) alkaline salt under stirring. But the order of addition can be exactly the other way round. The stirring is conducted until a homogeneous slurry is obtained.

[0026] The addition of the at least one natural polymer to the slurry obtained in step i) occurs under homogenization. The addition can be done by adding the complete amount of the at least one natural polymer all at once, or bit by bit over a certain period of time. The homogenization in step iii) does not differ from the homogenization of step ii) and is conducted after completion of addition of the at least one natural polymer. The time for the homogenization in step iii) can be chosen such that a homogeneous composition is obtained. This can take e.g. 1 minute, or 2 minutes, or 10 minutes, or 20 minutes or even more.

[0027] Mixing and homogenizing can be conducted in conventionally used equipment for mixing and homogenizing the components of the printing paste according to the invention, in particular for mixing and homogenizing components for pastes, e.g. an ultra-shear mixing blade or a high speed mixer or an immersion blender. The mixing and homogenizing of the components can be conducted for any suitable time at any suitable stirring rate, for example for 5 to 30 minutes at a stirring speed of 200 rpm to 4000 rpm.

[0028] The swelling step iv) is conducted for at least 5 minutes, or for at least 10 minutes, or for at least 15 minutes, or for at least 20 minutes, or for at least 25 minutes, or for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 90 minutes, or for at least 120 minutes, or for at least 150 minutes, or for at least 15

least 170 minutes, or for at least 200 minutes, or for at least 240 minutes. Step iv) starts, when step iii) is finalized. For step iv) the homogenized composition of step iii) is just left standing, i.e. no stirring or the like is conducted.

[0029] Optional step v) is only conducted if the printing paste should be colored or if the printing paste should be provided with gloss.

[0030] Further, the present invention relates to the use of the printing paste according to the invention or as manufactured according to the invention for printing a substrate.

[0031] For printing the substrate any suitable means or processes can be used, e.g. painting, textile printing methods, silk screen printing methods, ink jet printing methods, offset printing methods, tampon printing methods, stamp printing methods.

[0032] The substrate can be selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics. The substrate can be in particular textile. The textile can comprise or consist of cellulose fiber material, cotton or regenerated cellulose such as viscose and lyocell, keratinous fibers, polyamide, or any fiber blends including these fiber materials with any other fibers known in the prior art as e.g. but not limited to polyester, polyaramid polyamide, polyacrylic, viscose, linen etc.

[0033] The present invention further relates to a method for printing a substrate with the printing paste according to the invention or as manufactured according to the invention, wherein the method comprises i) printing the printing paste onto the substrate to obtain a printed substrate; ii) drying the printed substrate.

[0034] In step i) of the method for printing a substrate any commonly known method for printing a substrate can be used as already outlined before. In step ii), the drying is conducted at a temperature of at least 25 °C, or at least 30°C, or at least 40°C, or at least 50°C, or at least 60°C, or at least 70°C, or at least 80°C, or at least 90°C, or at least 100°C, or at least 120°C, or at least 120°C, or at least 130°C.

[0035] The invention further relates to a substrate printed with the printing paste according to the invention, or as manufactured according to the invention. Further the invention relates to a substrate as obtained according to the method for printing the substrate as claimed herein. As already defined before, the substrate can be selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics. The substrate can be in particular textile. The textile can comprise or consist of cellulose fiber material, cotton or regenerated cellulose such as viscose and lyocell, keratinous fibers, polyamide, or any fiber blends including these fiber materials with any other fibers known in the prior art as e.g. but not limited to polyester, polyaramid polyamide, polyacrylic, viscose, linen etc.

[0036] Further, the present invention relates to a method for removing the printing paste according to the invention or the printing paste as manufactured according

to the invention from the printed substrate according to the invention or as obtained according to the method for printing the substrate according to the invention. Said method comprises step i) subjecting the printed substrate to a cleaning step, wherein in the cleaning step water and at least one cleaning agent is used.

[0037] The term "cleaning agent" means within the context of the present application a substance e.g. a fluid, capable for flushing solid and/ or soluble residues, in particular the printing paste according to the invention, from the substrate. Typically, a cleaning agent is based on an aqueous fluid comprising detergents, like laundry detergents. Also, a soap can be used as cleaning agent. The cleaning step can comprise one or more of the following procedures: cold rinse, warm rinse, and/or soaping.

[0038] The cleaning step can be conducted in a normal washing machine, or any other commonly known suitable machine or equipment for cleaning the substrate.

[0039] The cleaning step is conducted for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 80 minutes, or for at least 90 minutes, or for at least 100 minutes, or for at least 110 minutes, or for at least 120 minutes.

[0040] The water used in the cleaning step can have a temperature of at least 25°C, or at least 30°C, or at least 35°C, or at least 40°C, or at least 45°C, or at least 50°C, or at least 55°C, or at least 60°C, or at least 65°C, or at least 70°C. In essence, the nature of the substrate determines the temperature of the water used during the cleaning step.

[0041] It is another advantage of the printing paste according to the invention, that the cleaning of the printed substrate onto which the printing paste is applied does not create problematic waste water. In fact, the waste water created during the cleaning step can be poured into the regular sink. It is another advantage of the printing paste according to the invention that the removal of the same from the printed substrate does not leave any or only very small residues of the printing paste on the printed substrate (see Figures). Thus, it is possible, to re-use the substrate and e.g. provide a new print onto the substrate.

EXAMPLES

[0042] The present invention is explained in more detail in the following examples, however, without being limited to these examples.

Example 1

Manufacturing of printing paste 1

[0043] 100 gr barytes (barium sulfate) are weighted. 600 g water are weighted. The temperature of the water is set to 30°C. The water is poured into the barytes under stirring. The stirring is continued until a smooth slurry is

obtained. The slurry is homogenized for 2 minutes using an immersion blender, 25 g of Klucel[™] H (available from Kremer Pigmente; hydroxypropyl cellulose) are weighted. Klucel[™] H is poured slowly over 1 minute into the slurry while the homogenization of the slurry is further conducted. When the addition of Klucel[™] H is complete, homogenization of the composition is continued for 10 minutes. Then, the thus obtained homogenized composition is allowed to stand and swell at room temperature for 240 minutes. Afterwards a light white printing paste is obtained, which is ready for use.

Example 2

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Manufacturing of printing paste 2

[0044] The procedure for manufacturing of printing paste 1 is repeated, with the sole difference that after the swelling step 72 g of green pigment (Aquaplast-DIY pigment concentrate may-green; color code: 60 from siebdruck-versand.de) is added into the composition. After the addition is completed, the composition is again homogenized to achieve a homogenous color of the printing paste. Thus, a green printing paste is obtained, which is ready for use.

Example 3

Manufacturing of printing paste 3

[0045] The procedure for manufacturing printing paste 2 is repeated with the difference that magnesia chalk (magnesium carbonate; Diaclean chalk from available from Diacleanshop) is used instead of baryte and that a yellow pigment (Aquaplast-DIY pigment concentrate neon-yellow; color code: 82 from siebdruck-versand.de) is used. Thus, a yellow printing paste is obtained which is ready for use.

Application Example 1

[0046] A dark grey t-shirt from organic cotton is used as substrate. The printing paste according to Example 1 is applied to the t-shirt by silk screen printing. After the application of the printing paste of Example 1 is finalized, the printing paste is subjected to a drying step at 120°C for 30 seconds in a drying tunnel. A light grey print is obtained on the t-shirt. Then, the procedure is repeated but using the printing paste according to Example 2. Thus, a green print is obtained on the t-shirt. Both prints do not completely overlap. The result of Application Example 1 is depicted in Figure 1 a.

Application Example 2

[0047] The procedure of Application Example 2 is repeated with the sole difference that the printing paste according to Example 3 is used. The printing paste 3 is

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also printed twice onto the t-shirt. Thus, a yellow print is obtained on the t-shirt. The result of Application Example 2 is depicted in Figure 2a.

Removing step

[0048] Both t-shirts (according to Application Example 1 and Application Example 2) are subjected to a cleaning step for removing the printing pastes in the washing machine, chosing a 40°C color wash programme of 100 minutes duration, adding 75g of organic detergent by Ecover, adding other textiles to have a loosely filled wash drum. [0049] After the washing step, the t-shirts were dried and inspected for residues of the printing pastes. As can be seen in Figures 1b (T-shirt according to Application Example 1) and 2b (t-shirt according to Application Example 2), there are no residues of the printing pastes left on the t-shirts.

Claims

- 1. Printing paste comprising
 - a) at least one liquid selected from water, alcohols or a mixture thereof;
 - b) at least one alkali metal salt or earth alkali metal salt selected from carbonates or sulfates or a mixture thereof;
 - c) at least one natural polymer selected from cellulose, cellulose derivatives, polysaccharides, collagens or mixtures thereof.
- 2. Printing paste according to claim 1, wherein the printing paste comprises additives selected from the group comprising proteins, fatty substances, sugars, waxes, pigments or mixtures thereof.
- 3. Printing paste according to claim 1 or 2, wherein the weight ratio of the at least one liquid to the at least one alkali metal salt or earth alkali metal salt to the at least one natural polymer is in the range of at least 10:4:1, or at least 12:4:1, or at least 15:4:1, or at least 20:4:1, or at least 24:4:1, and at most 100:16:1, or at most 96:16:1, or at most 90:16:1, or at most 50:8:1, or at most 48:8:1.
- **4.** Printing paste according to at least one of claims 1 to 3, wherein the printing paste comprises
 - a) water;
 - b) earth alkali metal carbonate or sulfate selected from calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), barium sulfate (BaSO₄) or a mixture thereof;
 - c) cellulose or cellulose derivates selected from methylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxypropylme-

- thyl cellulose, ethylmethyl cellulose, carboxymethyl cellulose or mixtures thereof; d) optionally at least one pigment.
- 5 5. Method for manufacturing the printing paste as claimed in at least one of claims 1 to 4 comprising the steps of
 - i) mixing the at least one liquid and the at least one earth alkaline salt to form a slurry;
 - ii) homogenization of the slurry obtained in step
 - i), while adding the at least one natural polymer;
 - iii) further homogenization of the composition obtained in step ii);
 - iv) swelling of the homogenized composition obtained in step iii) to obtain the printing paste;
 - v) optionally mixing and homogenizing at least one additive.
 - **6.** Method as claimed in claim 5, wherein step iv) is conducted for at least 5 minutes, or for at least 10 minutes, or for at least 15 minutes, or for at least 20 minutes, or for at least 25 minutes, or for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 90 minutes.
 - Use of the printing paste according to at least one of claims 1 to 4 or use of the printing paste as manufactured according to claims 5 or 6 for printing a substrate.
 - **8.** Use as claimed in claim 7, wherein the substrate is selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics; preferably textile.
 - 9. Method for printing a substrate with the printing paste according to at least one of the claims 1 to 4 or with the printing paste as manufactured in claims 5 or 6 comprising:
 - i) Printing the printing paste onto the substrate to obtain a printed substrate;
 - ii) Drying the printed substrate.
 - 10. Method as claimed in claim 9, wherein the drying is conducted at a temperature of at least 25 °C, or at least 30°C, or at least 40°C, or at least 50°C, or at least 60°C, or at least 70°C, or at least 80°C, or at least 90°C, or at least 100°C, or at least 110°C, or at least 120°C, or at least 130°C.
 - 11. Substrate printed with the printing paste as claimed in at least one of the claims 1 to 4 or the printing paste as manufactured in claims 5 or 6; or substrate as obtained according to the method as claimed in claims 9 or 10.

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12. Substrate as claimed in claim 11, wherein the substrate is selected from glass, paper, cardboard, leather, textile, metal, wood, stone, plastics; preferably textile.

13. Method for removing the printing paste as claimed in at least one of the claims 1 to 4 or the printing paste as manufactured in claims 5 or 6 from the printed substrate as claimed in claims 11 or 12, or as obtained according to the method claimed in claims 9 or 10 comprising

i) subjecting the printed substrate to a cleaning step, wherein in the cleaning step water and at least one cleaning agent is used.

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14. Method according to claim 13, wherein the cleaning agent is selected from soaps or laundry detergents, or mixtures thereof.

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15. Method according to claim 13 or 14, wherein the cleaning step is conducted for at least 30 minutes, or for at least 40 minutes, or for at least 50 minutes, or for at least 60 minutes, or for at least 70 minutes, or for at least 80 minutes, or for at least 90 minutes. or for at least 100 minutes, or for at least 110 minutes, or for at least 120 minutes.

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Figure 1a

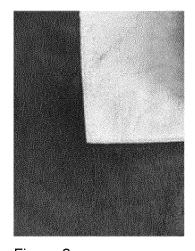


Figure 2a

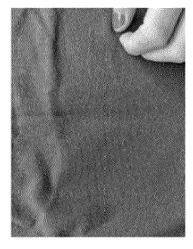


Figure 1b



Figure 2b



EUROPEAN SEARCH REPORT

Application Number

EP 23 16 5717

1	0	
	•	

	DOCUMENTS CONSIDERED	TO BE RELEVANT		
Category	Citation of document with indication of relevant passages	, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
x	EP 3 390 710 B1 (LAMBERT 30 October 2019 (2019-10 * paragraphs [0061] - [0 * claim 1 *	-30)	1-3,5-15	INV. D06N3/00 D06N3/02 D06P1/50 D06P1/673
x	EP 0 909 766 A2 (BORCHER 21 April 1999 (1999-04-2 * paragraphs [0029] - [0 * claim 5 *	1)	1–6, 13–15	D06P5/13
x	CN 108 951 227 A (SHANDO CHEMICAL CO LTD) 7 December 2018 (2018-12 * example 1 *		1–15	
x	CN 115 075 026 A (GUANGZ CO LTD) 20 September 202 * example 1 *	2 (2022-09-20)	1–15	
			_	TECHNICAL FIELDS SEARCHED (IPC)
				D06N D06P D06M D06Q C09D
	The present search report has been dra	wn up for all claims Date of completion of the search		Examiner
	The Hague	27 September 2023	Que	ste, Sébastien
X : part Y : part doci	ATEGORY OF CITED DOCUMENTS icularly relevant if taken alone icularly relevant if combined with another ument of the same category inological background	T: theory or principle u E: earlier patent docur after the filing date D: document cited in tl L: document cited for o	ment, but publis he application other reasons	nvention hed on, or

EP 4 438 803 A1

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 23 16 5717

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

CN

EР

ES

WO

BR

ΕP

JP

NONE

NONE

Patent family

member(s)

108368674 A

2017102870 A1

3390710 A1

2770327 T3

9803903 A

0909766 A2

H11228601 A

27-09-2023

Publication

date

03-08-2018

24-10-2018

01-07-2020

22-06-2017

14-12-1999

21-04-1999 24-08-1999

10		Patent document cited in search report			Publication date	
		EP 339	90710	в1	30-10-2019	
15						
		EP 090	9766	A2	21-04-1999	
20						
			3951227 		07-12-2018	
		CN 115	5075026 	A 	20-09-2022	
25						
30						
35						
40						
45						
40						
50						
	1459					

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82